

The Production of High B.t.u. Gas from Light Petroleum
Distillate by Low Temperature Catalytic Steam Reforming

Robert G. Cockerham
George Percival

Gas Council, Midlands Research Station
Solihull, U.K.

Summary

This paper describes processes for the production of high calorific value gas by the steam reforming of light petroleum distillate under pressure at low temperature. The distillate is first purified and then gasified to a methane-rich gas over a catalyst at 500°-550°C. At this temperature carbon deposition is avoided and steam-distillate ratios approaching the theoretical minimum can be employed. After carbon dioxide removal, the product gas would have a calorific value of 800-850 B.t.u./cu.ft.

The methane-rich gas which is non-toxic and free of sulphur may be methanated at about 350°C. The re-establishment of equilibrium at this lower temperature produces a gas, which after the removal of carbon dioxide, contains over 95 per cent of methane. The calorific value of this gas would be 950 B.t.u./cu.ft. With butane, high calorific value gas can be produced in one stage.

Results are given for experimental work in the laboratory and on a pilot plant in which the feedstock varied from butane to distillates boiling up to 170°C.

I Introduction

Work on the catalytic gasification of light distillate began at the Midlands Research Station of the Gas Council in 1956¹. The investigation was designed to develop a process for the manufacture of a gas with a calorific value of 500 Btu per cu.ft. for peak load use alongside coal gasification plant operating at pressure. A primary consideration was plant cost and therefore an autothermic system was chosen which required the introduction of air for internal combustion.

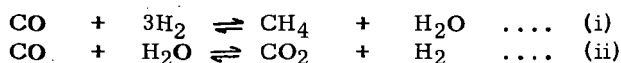
The early laboratory work indicated that steam economy and a high thermal efficiency would be more readily achieved if the transition from distillate to town gas were made in two principal stages. In the first, steam and distillate reacted at about 500°C over a highly active catalyst to give a gas rich in methane and, in the second, a reforming reaction reduced the methane content of the gas to the level required for town gas. The temperature of the first stage was maintained by the exothermic formation of methane whilst the combustion of air supplied to the second satisfied the thermal requirement of the reaction between the methane and steam.

It is the gasification of the distillate in the first stage which provides the substance of this paper, however, since gas of up to 350 Btu/cu. ft. calorific value can be prepared by it. Still higher calorific values can be achieved by methanating the gas obtained.

II The Catalytic Gasification of Distillate at Pressure

(a) Laboratory Experiments on Process Design

When hydrocarbons are gasified with steam in the presence of a catalyst the gas produced consists of methane, hydrogen, carbon monoxide and carbon dioxide. Provided that the catalyst is sufficiently active the following reactions are brought to equilibrium:



At equilibrium, the gas composition is determined by the reaction conditions, so that for a given ratio of steam to hydrocarbon the gas becomes richer in methane as the working pressure is raised and the reaction temperature is lowered. As the system moves towards methane the steam requirement falls and the overall reaction becomes exothermic. Conditions may be chosen, therefore in which it is possible to convert a hydrocarbon feedstock to a methane rich gas continuously, the heat of reaction being sufficient to provide for heat losses from the system.

Laboratory experiments showed that a temperature within the range 400-550°C eliminated the danger of depositing carbon by the thermal decomposition of the hydrocarbon before reaction with steam. In order to establish equilibrium at these temperatures it was necessary to use a very active catalyst and to free the feedstock from sulphur compounds to avoid poisoning it. The composition of the gas produced when distillate was gasified with twice its weight of steam at 500°C. and under a pressure of 25 atmospheres is given in Table 1.

A process was envisaged, therefore, in which vaporized hydrocarbon in the form of liquified petroleum gas or light distillate was freed from sulphur compounds, mixed with steam, preheated and supplied under pressure to a suitable catalyst. The removal of sulphur from the feedstock eliminates the need for gas purification and safeguards catalysts that are used in subsequent reactions. The low temperature employed allows the steam requirement to be reduced to the minimum and increases the thermal efficiency of the process. Approximately 1.05 therms of methane-rich gas are produced per therm of light distillate supplied and, if heat recovery is practised, an overall thermal efficiency of 95% can be achieved. The flow diagram of the process shown in Fig. 1. includes the purification of the feedstock, gasification and the removal of carbon dioxide. A small proportion of the scrubbed gas is recycled to provide hydrogenating gas for the purification section.

Table 1 The Composition of Gas Produced at 500°C and 25 Atmospheres

	Wet	Dry	Calculated to CO ₂ = 1%
Gas Composition, per cent by volume.			
CO ₂	10.4	20.6	1.0
CO	0.35	0.7	0.85
H ₂	8.45	16.8	20.95
CH ₄	31.2	61.9	77.2
H ₂ O	49.6	-	-
Calorific Value, Btu. per cu.ft.		671	836
Equivalent Temperatures for the equilibria, °C.			
CO + 3H ₂ ⇌ CH ₄ + H ₂ O	496		
CO + H ₂ O ⇌ CO ₂ + H ₂	500		

(b) The Purification of the Feedstock

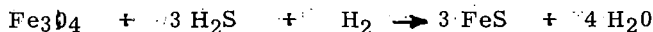
The amount of sulphur in light distillates available in the U.K. is within the range 100-500 p.p.m. by weight. In low boiling fractions mercaptans and disulphides are present, but in the higher boiling materials heterocyclic sulphur compounds may be found.

Early experiments showed that the removal of sulphur compounds from distillate in the liquid phase was unlikely to be successful and that a chemical method, applicable to all types of sulphur compound was essential to achieve a satisfactory degree of purity.

Absorption of sulphur from distillate in the vapour phase, at pressure, was therefore attempted, using alkaline iron oxide in the manner in which it has been used for synthesis gas. This reagent operates by a mechanism which involves conversion of sulphur compounds to hydrogen sulphide, and the presence of a trace of oxygen in the gas facilitates absorption as sulphur oxides in the alkali. Oxygen could not be used with distillate with which it reacts preferentially although, when hydrogen was added to the distillate vapour, iron oxide had an adequate capacity to absorb the sulphur as hydrogen sulphide without oxidation. It was found that the sulphur compounds could be more effectively hydrogenated by treatment separately over a molybdenum based catalyst at 350 - 400°C. The process thus developed as the vaporization of the distillate, admixture of hydrogenating gas, the conversion of sulphur compounds over a molybdenum catalyst and the absorption of the hydrogen sulphide formed in iron oxide.

Commercial molybdenum catalysts supported on alumina were found to be suitable for the conversion step, when about half a cubic foot of hydrogen was

used per pound of distillate. Luxmasse, widely used for synthesis gas purification ⁵⁵ was retained as it is a powerful absorber of hydrogen sulphide at elevated temperature; it is porous and there is rapid diffusion into the interior of granules. Prepared forms are of necessity of lower porosity, but this is of little account since absorber vessels are designed for relatively long periods of operation. The crude material contains approximately 6% of alkali and approximately 50% by weight of iron oxide as ferric oxide. There is evidence however that under working conditions conversion to hydrated magnetic oxide of iron occurs and sulphur absorption proceeds according to the equation:-



After treatment, the amount of sulphur in distillate was very small, in all cases less than one part per million, and a special analytical technique was required to measure it accurately. A combustion procedure described by Wickbold ² proved satisfactory, the sulphur being finally estimated by nephelometric titration with 0.0025M. barium chloride.

The amount of hydrogen added is many times the quantity theoretically required for reaction with the sulphur compounds in order to displace the equilibrium towards hydrogen sulphide. In some cases even more would be required, because it was found that if olefins were present in the distillate they were hydrogenated, although aromatics in the distillate were unchanged after processing. The quantity of olefins in the distillates available was insufficient to show this directly, but distillates from olefinic crudes were simulated by the addition of n-hexene and n-heptene, and styrene was employed to represent the effect of blending in fractions from cracked stocks.

The process described has been applied to a number of distillates ranging from butane, containing 0.6 per cent of butenes and 8 parts per million of sulphur, up to kerosene, containing 3 per cent of olefins and 1000 parts per million of sulphur. With the higher gravity distillates, it was necessary to increase the hydrogen supply and temperature.

In reforming processes, make gas is usually used as the hydrogenating gas for purification and this practice can be followed when making rich gas, if the volume recycled is increased to compensate for its low concentration of hydrogen. Carbon dioxide should be removed to below 5 per cent since it interferes with the purification.

(c) Further Laboratory Experiments on the Gasification Reaction

After purification, the gasification process outlined operated satisfactorily in the laboratory with butane and low-boiling types of distillate using in the gasification stage a co-precipitated nickel-alumina catalyst formulated for methane synthesis. ³ Further development of the catalyst has since been necessary, however, since with distillates of higher specific gravity and boiling point, it was found that there was a tendency for the catalyst to lose activity. The reaction zone would increase in length during an experiment until it extended to the full depth of the catalyst bed and

undecomposed distillate would then appear in the product gas.

Considerable evidence has now been collected which indicates that the deactivation with higher boiling distillates is due to the formation of a polymer which reduces the accessibility of the reacting molecules to the surface of the catalyst. The work of Kemball⁴ throws light on a possible mechanism involving the production of radicals on the catalyst surface which may either react with steam or link together to form polymer. There is a difference between this polymerisation and the deposition of carbon, however. The latter depends upon the complete breakdown of distillate molecules to carbon atoms which appear to enter the catalyst structure and crystallize from there leaving the surface active. This process can continue until there is a blockage, whereas no increase in back pressure is observed during the deactivation of catalyst by polymer.

The regeneration of deactivated catalysts has been only partly successful. Oxidation processes which will remove the polymer also damage the catalyst and the original level of activity cannot be restored. Treatment with hydrogen at the working temperature will re-activate a recently poisoned surface. The object of the experimental work, however, has been to minimise polymer formation and the stage has now been reached where the loss of catalyst activity has been reduced to negligible proportions with the distillates available.

This has been achieved by modifying the catalyst composition, using an optimum preheat temperature for the distillate and paying attention to the rates of supply of feedstock and steam to the catalyst bed. Distillate having a boiling point of 170°C. can be gasified satisfactorily and it is estimated that the life of the catalyst in a commercial plant will be at least one year and possibly up to five years.

Experiments are continuing with feedstocks of higher boiling point and in the laboratory it has been found possible to gasify kerosene.

(d) The Steam Requirement

Since the amount of steam used in all reforming processes is an item which affects both the thermal efficiency and the operating costs, it has been the practice during the present investigations to keep the amount near the theoretical minimum. The minimum is governed by the fact that catalysts not only establish the methane-steam and water gas equilibria but also promote the Boudouard reaction:



Carbon will tend to be deposited by this reaction if the concentration of carbon monoxide in the gases exceeds the value corresponding to the equilibrium. Control can be exercised by allowing an excess of steam to limit the carbon monoxide/dioxide ratio according to the water gas reaction. The minimum amount of process steam required to prevent carbon deposition by this reaction can therefore be calculated from the equilibrium constants.

Fig. 2 shows the curves for the minimum steam requirement for hexane when reformed at various pressures. Although the curves pass through a maximum and then fall again at the highest temperatures, the latter values are not attainable

in practice since the system would inevitably have been taken through the lower temperatures. The curves indicate that at a temperature of 530°C for example, and under a pressure of 20 atmospheres the minimum steam-hexane ratio is 1.0 parts by weight. These are similar to the conditions which are employed in the gasification stage of the process but allowance must be made for the composition of distillate feedstocks and a margin provided against accidental fluctuations. A steam-distillate ratio of 1.2 has been satisfactory in the laboratory but, for the commercial production of rich gas under pressure, a ratio of 1.5 would be regarded as the minimum for distillates boiling up to 170°C. It will be noted that steam ratios of 1.6 and 2.0 have been used on the pilot plant but this is because in the U.K. the rich gas has subsequently to be reformed at a higher temperature in order to reduce its calorific value to 500 Btu/cu.ft. The effect of varying the proportion of steam supplied on the composition of the gas produced is given in Table 2.

TABLE 2

The Effect of Varying the Proportion of Steam on the Composition of the Gas Produced at 540°C and 25 atmospheres

Steam supplied, lbs/lb distillate	1.2	1.6	2.0
Gas Composition, dry, per cent by volume			
CO ₂	22.55	22.85	22.95
CO	2.0	1.75	1.55
H ₂	12.5	16.15	19.25
CH ₄	62.95	59.25	56.25
Gas Composition, dry, calculated to 1.0% carbon dioxide, per cent by volume.			
CO ₂	1.0	1.0	1.0
CO	2.55	2.25	2.0
H ₂	16.0	20.7	24.75
CH ₄	80.45	76.05	72.25
Calorific Value, Btu/cu.ft.	859	829	803

(e) Pilot Plant

The pilot plant in operation at Solihull is shown in Fig. 3. It has an output of 1/5 million cu.ft. of town gas per day. From the left, the three short vessels constitute the distillate purification section followed by the catalytic gasifier, second reforming stage for town gas, carbon monoxide converter and final cooler, in that order. No provision was made for removing carbon dioxide from the gas since this was regarded as an established operation and gas compositions can be readily adjusted.

The pilot plant was designed to have catalyst beds of a similar depth

to those of a commercial plant and, therefore, at a given space velocity, the linear velocity of the reactants through the beds is full scale. Scaling up then involves an increase in reactor diameter only and it is believed that large units can be designed from test results with confidence. For this reason the pilot reactors are long, of small diameter and liable to heat loss from the walls. This was prevented by the use of electrically heated lagging. No heat exchangers were used on the pilot plant, the preheating of the distillate vapour prior to purification and of the process steam being carried out in gas fired equipment.

The control of the plant during tests involved maintaining constant preheat temperatures to both the purification and the gasification sections and adjusting the steam supply to give the appropriate ratio. The preheat temperature to the gasification catalyst was 440°C when butane was used and varied from 460° to 535°C in the case of distillate feedstocks. The tests have normally lasted at least a month in order to obtain an indication of the life of the gasification catalyst. Observations of the movement of the reaction zone are made with a system of thermocouples.

Table 3 gives a selection of results covering different feedstocks, steam ratios and pressures.

TABLE 3
The Results of Pilot Plant Tests

Test No.	1	2	3
Type of Distillate, F.B.P., °C.	170	115	Butane
Pressure, atmospheres	20	20	25
Process Steam, lb. per lb of feedstock	1.6	1.6	2.0
Temperatures, °C Inlet catalyst	515	515	440
Outlet catalyst	553	550	487
Gas Composition, per cent by volume	Wet Dry	Wet Dry	Wet Dry
CO ₂	14.4 21.9	13.0 20.5	9.2 18.5
CO	1.0 1.5	1.0 1.55	0.3 0.6
H ₂	12.6 19.15	12.0 18.95	7.5 15.1
CH ₄	37.8 57.45	37.4 59.0	32.7 65.8
H ₂ O	34.2 -	36.6 -	50.3 -
Calorific Value, Btu. per cu.ft.	637	652	704
Gas Composition, dry, calculated to 1.0% carbon dioxide, per cent by volume			
CO ₂	1.0	1.0	1.0
CO	1.9	1.95	0.7
H ₂	24.25	23.6	18.35
CH ₄	72.85	73.45	79.95
Calorific Value, Btu per cu.ft.	807	811	855
Specific Gravity (Air = 1.0)	0.454	0.457	0.462
Gas Yield (CO ₂ =1%)s.cu.ft. per lb feedstock	26.6	26.7	25.7
Therms in gas	1.06	1.06	1.0
Therms in feedstock			

The effect of changing the feedstock can be seen by comparing Tests 1 and 2 in which distillates boiling up to 170°C and 115°C respectively were used under identical conditions of pressure, preheat temperature and steam ratio. The concentration of carbon dioxide is lower in the gas produced from the lighter distillate whilst the methane content of the scrubbed gas is higher at 59.0 per cent. Test 3 was carried out using butane at 25 atmospheres pressure and with a steam ratio of 2.0. The low preheat temperature of 440°C gives rise to a high concentration of methane in the product gas.

Calculated gas compositions are given in which carbon dioxide has been removed to one per cent. It will be seen that the calorific values of the resultant gases would lie in the range 807 to 855 Btu per cubic foot.

A commercial plant is being built for the production of 25,000 therms per day of methane-rich gas at 17 atm. pressure from a distillate feedstock.

(f) The Production of Gas Interchangeable with Natural Gas

Although the process so far described is capable of producing a gas having a calorific value of up to 850 Btu per cu. ft., the presence of hydrogen raises the flame speed above the level of certain natural gases. In order to be interchangeable with natural gas, therefore, the equilibrium needs to be established at as low a temperature as possible. When liquefied petroleum gases are used as the feedstock the reaction with steam may be carried out at a temperature between 300°C and 400°C. Gas of the following composition was produced when butane was gasified at 25 atmospheres pressure using a steam-butane ratio of 1.3 by weight :-

CO₂ 17.75, CO 0.05, H₂ 1.8, CH₄ 80.45 per cent by volume.

After the removal of carbon dioxide this gas would contain 96.55 per cent of methane and have a calorific value of 970 Btu/cu. ft. With high boiling distillate, however, the temperature of the gasification stage cannot be reduced to this low level without causing deterioration of the catalyst, but a subsequent methanation stage can be used.

The pilot plant was equipped with an auxiliary methanation tube through which gas from the gasification catalyst was passed at 360°C and 25 atmospheres pressure. If carbon dioxide had been removed, the dry gas produced would have had the following composition, per cent by volume :-

CO₂ 1.0, CO 0.3, H₂ 0.7, CH₄ 98.0, Calorific Value = 977 Btu per cu. ft.

When two stages are used it is convenient to condense some of the undecomposed steam as an intermediate step in order to raise the concentration of carbon oxides in the reaction zone. The scale of the experiment was not large enough for the problem of heat removal from the catalyst bed during methanation to be encountered. There are a number of ways in which this may be done, but a discussion of these techniques is outside the scope of this paper. When operating at 25 atm. pressure, 1 therm of methane can be produced from 0.98 therms of distillate at a thermal efficiency of 95%.

Acknowledgments

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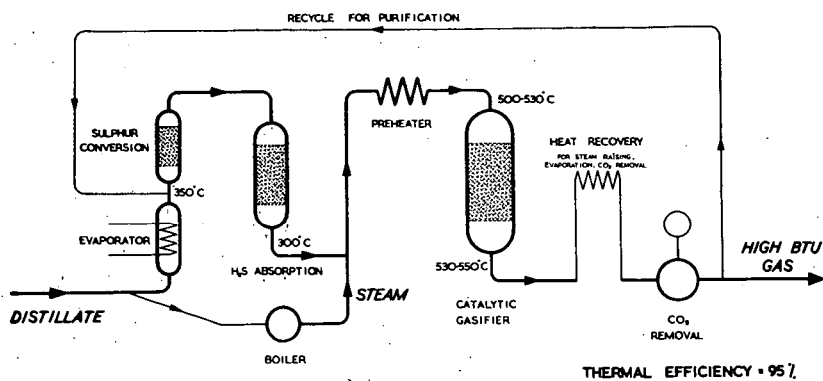


Fig. 1. Flow Diagram of the Gasification Process

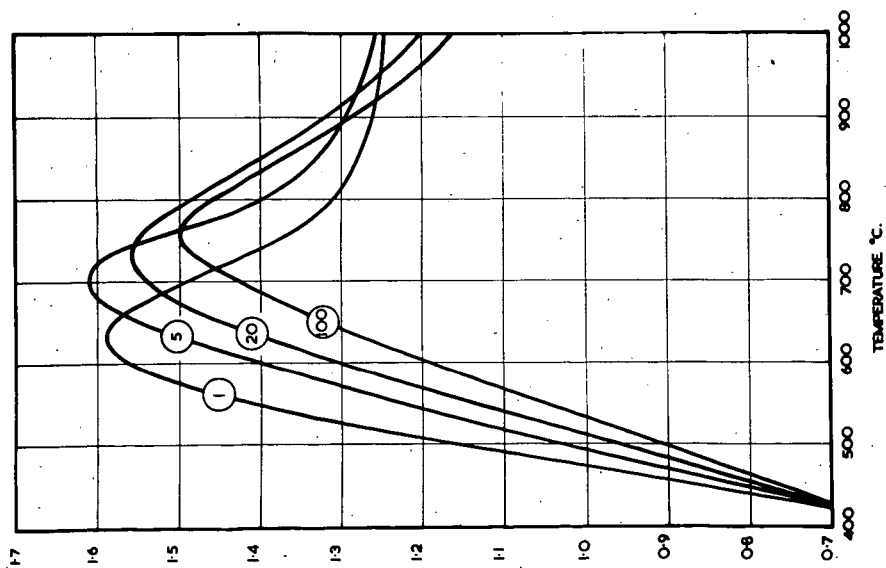


Fig. 2. Minimum Steam Requirement for the Gasification of Hexane at Various Temperatures (Pressures in atmospheres are shown on the curves)

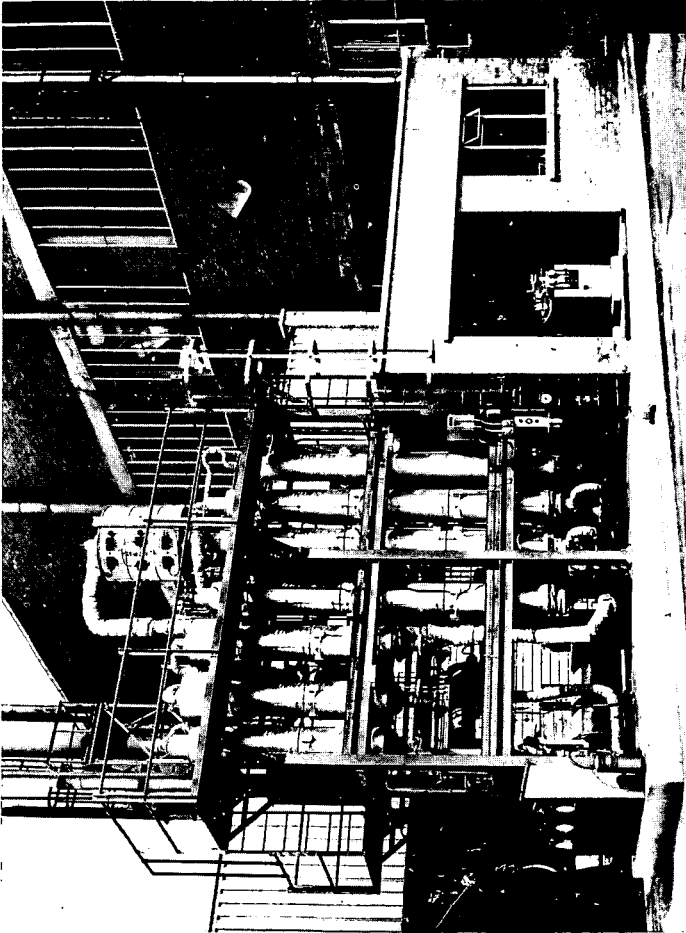


Fig. 3. The Pilot Plant for the Gasification Process